ELECTRICAL WIRE INSULATION

Ins. A1

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This invention relates to insulation for electrical wire or cable (hereinafter "wire") in which a strong bond is achieved at an interface between a layer of polyolefin-based material and a layer of polyvinylidene fluoride-based material. The invention is especially useful in multi-layer insulation of electrical wires, making it possible to achieve high-performance bonding between layers of such materials while retaining an acceptable balance in the complex relationships of other wire performance requirements, which are specialised and different from the criteria for other kinds of article such as mouldings or packaging films.

The following abbreviations will be used hereinafter:
PJ = Primary jacket; pro-rad = crosslinking promoter; TMPTM = trimethylolpropanetrimethacrylate; ASTM = American Society for Testing and Materials; PVDF = polyvinylidene fluoride; VDF = vinylidene fluoride; HFP = hexafluoropropylene;
HDPE = high density polyethylene; EEA = ethylene/ethyl acrylate;
EMA = ethylene/methyl acrylate; EVA = ethylene/vinyl acetate; EA = ethyl acrylate;
MA = methyl acrylate; VA = vinyl acetate.

Ins A2

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Dual wall wire insulation comprising a polyolefin inner layer (core) and polyvinylidene fluoride (PVDF) outer layer (primary jacket or PJ) has been commercially available for over 30 years, and is available from several different manufacturers. These products all have negligible adhesion between the inner (polyolefin) and outer (PVDF) layers, which are consequently easily separable. It has been necessary to accept certain disadvantages arising from this lack of bonding, which limits the robustness of the construction. For example, the outer insulation layer can crack and peel off the inner layer if subjected to mechanical stress, exposure to certain fluids, contact with sharp objects, or impact. Abrasion and flexural fatigue resistance of the insulation, as well as resistance to wrinkling on bending (which can cause difficulties in sealing the wire or inserting it into grommets or connectors) are also detrimentally affected by having two readily separable insulation layers. It has not been thought possible to bond layers of two such dissimilar classes of

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material as polyolefins and PVDFs on a wire at commercially acceptable cost and manufacturing efficiency. Moreover, available bonding techniques could unacceptably affect the wire performance characteristics. The conventional approach to the bonding of polyolefins and PVDF is to employ a tie layer material (e.g. US patent 5,589,028), but these tend to be expensive, and when used on wire may compromise other properties, e.g. heat ageing, and add complexity to the manufacturing process in forming the extra layer. They may also be of limited effectiveness in terms of the bond strength developed.

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It has now been discovered, according to the present invention, that the dissimilar insulation materials of a polyolefin-based core and a polyvinylidene fluoride-based PJ can be bonded together to a significant level of adhesion on an electrical wire or cable; that this bonding tends to reduce or eliminate the aforementioned robustness problems on a wire; and that this bonding can be achieved, contrary to expectation, without unacceptable effects on crack propagation resistance, cost, or on the general balance of wire performance characteristics.

In the wire or cable insulation according to the present invention, significant bond strength is unexpectedly achieved by a combination of a selected formulation of a polyolefin-based layer, in contact with a polyvinylidene fluoride-based layer, and a cross-linking reaction, preferably effected by the application of radiation, especially ionising radiation.

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The invention accordingly provides an electrical wire having insulation comprising:

(i) at least a first layer of a polyolefin-based material comprising, of which at least 20%, preferably at least 40%, more preferably at least 60% or at least 80%, by weight (of the whole material composition) of a carbonyl-containing polymer (homopolymer or copolymer or terpolymer) having a non-aromatic backbone, of which polymer the or at least one constituent monomer is a carboxylic acid ester, preferably an acrylate or acetate, especially an alkyl acrylate (preferably methyl acrylate, ethyl acrylate, propyl acrylate or butyl acrylate), the said monomer itself constituting at least 5%, preferably at least 9%, more preferably at least 15% by weight of the said co-, or ter- polymer when used, and the remainder of the said co-, or ter- polymer preferably being derived from olefinic monomer, preferably ethylene, in contact with;

(ii) at least a second layer of a material containing at least 10%, more preferably at least 50%, or at least 90%, by weight of polyvinylidine fluoride (PVDF), or especially preferably a copolymer based on VDF with a partially or fully fluorinated co-monomer, most preferably a copolymer of VDF and hexafluoropropylene (HFP);

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wherein the said layers (i) and (ii) whilst in contact with each other have been subjected to cross-linking reaction, preferably by radiation, more preferably ionising radiation, sufficient to increase the peel bond strength between the said layers to at least 5N, preferably increasing the bond strength by at least 50%, more preferably by at least 100%, especially by at least 500% or 1000%, compared to that between the uncrosslinked layers.

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According to another aspect of the invention, we provide an electrical wire having insulation comprising:

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(i) at least a first layer of a polyolefin-based formulation, of which at least 20%, preferably at least 40%, more preferably at least 60% or very preferably at least 80% of the weight of the polymeric portion of the said formulation consists of a carbonyl-containing polymer (homopolymer or copolymer or terpolymer), of which polymer the or at least one constituent monomer is a carboxylic acid ester, preferably an acrylate or acetate, especially an alkyl acrylate (preferably methyl acrylate, ethyl acrylate, propyl acrylate or butyl acrylate), the said monomer itself constituting at least 5%, preferably at least 9%, more preferably at least 15% by weight of the said co-, or ter- polymer when used, and the remainder or the majority of the remainder of the said co-, or ter- polymer preferably being derived from olefinic monomer, preferably ethylene; in contact with

(ii) at least a second layer of another material formulation, containing at least 10%, more preferably at least 50%, very preferably at least 90%, especially 100%, by weight of the second layer, of polyvinylidine fluoride (PVDF), or especially preferably of a copolymer based on VDF with a partially or fully fluorinated co-monomer, most preferably a copolymer of VDF and hexafluoropropylene (HFP);

wherein the said layers (i) and (ii) whilst in contact with each other have been subjected to cross-linking reaction, preferably by radiation, more preferably ionising radiation, sufficient to prevent delamination of the two layers during the acetone immersion test

described below, or to increase the peel bond strength between the said layers to at least 5N according to the ASTM B1876-95 method described below preferably increasing the bond strength by at least 50%, more preferably by at least 100%, especially by at least 500% or 1000%, compared to that between the uncrosslinked layers.

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Preferably, the respective layers have been brought into contact with each other at a temperature above the melting or softening point of the polymeric material in at least one of the layers, thus tending to maximise the intimacy of their interfacial contact and so possibly encouraging the formation of adhesion-promoting interfacial cross-links in the subsequent cross-linking reaction.

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The polyolefin-based layer (i) in addition to the polymeric portion of the formulation, for which the requirements are stipulated above, may contain whatever else is required in the way of additives such as anti-oxidants, pigments, fillers, flame retardants, etc, as known per se, to give the required mechanical, thermal, electrical etc. properties to the polymer.

The polyvinylidene fluoride-based layer (ii) also may contain other additives as known per se to give it required properties in addition to bonding.

Advantages of achieving a strong bond in accordance with this invention include:

- abrasion resistance of surface layer, and the insulation as a whole can increase if it (the surface layer) is bonded to a substrate material;
- improved resistance to peel, especially if one of the layers is damaged/perforated;
- improved resistance to blistering of the two layers, if heat is applied;
- improved resistance to delamination/creasing/wrinkling between the two layers, e.g. due to mechanical stress or chemical exposure e.g. to solvents.
- achievement of reduced wire bend wrinkling and improvement in the above characteristics, while maintaining adequate cut-through and notch propagation resistance, the latter being unexpected since strongly adherent layers would normally be expected fairly easily to transmit a cut or notch in the outer layer through to the inner layer.

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The bond strength described in this application can be measured in terms of peel strength between bonded strips of the two materials in question. A standard method which can be used for such a test is ASTM 1876-95. By this definition, a significant bond could be one for which the peel force exceeds 5N, and a strong bond one of peel force greater than 10N. A convenient method for gauging the bond strength between the said layers, (i) and (ii), when they have been fabricated onto a wire, is to place a sample wire, of total length 60mm, into acetone (e.g. Fisher Scientific UK, AR certified grade acetone), to a depth of acetone equivalent to 70% of the length of sample wire, at 23 (+/- 3)°C, for a period of 1 hour. Wires with negligible bonding of the insulation layers experience an extension of the PVDF PJ, along the axis of the wire, that is independent of any extension of the polyolefin core, and/or wrinkling of the PJ such that it delaminates from the core in places. When it occurs, the above-mentioned extension of the PJ typically results in a PJ "tube" extending for 1mm or more beyond the cut end of the core in the sample wire, following the above test. Wires with significantly bonded insulation layers experience an extension of the core and PJ, together, without separation, beyond the cut edge of the conductor, along the axis of the wire and/or wrinkling of the core and PJ layers together, without delamination. Any such wrinkling of the core and PJ together can be distinguished from wrinkling of the PJ only by examining a cross-section of the wrinkles under a microscope.

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Methods of fabricating the wire may include any process which causes intimate contact between the above-mentioned layers (i) and (ii). Examples include coating of one material onto a pre-formed layer of the other, dual or multi-walled extrusion to form insulation layers respectively containing one or other of the aforementioned two classes of material. The olefin-based material (i) is preferably the inner layer and the PVDF-based layer (ii) preferably the outer layer on the wire. The layers made from the two different materials could be coextruded, tandem extruded, multipass extruded, or coated by other means. Known wire insulation processes such as tube draw-down extrusion may be used, to form one or more of the layers, but pressure extrusion as known per se is preferred for optimum adhesion of the second and any subsequent insulation layers to be applied to a pre-formed underlying layer.

The insulation on the wire is exposed to a cross-linking reaction, which may involve chemical reagents such as peroxides, but preferably is effected by radiation, especially from a source of ionising radiation capable of causing the formation of free radicals and thus, cross-links, in the polymers, some of which should preferably be formed in the region of the interface between the two materials. Penetration of the radiation into the material at least as far as the interface is therefore desirable, although not necessarily essential if ion or radical mobility, for example, enables molecular reactions to continue at or near the interface after the radiation process. The radiation source could, for example, be a radio-isotope, or an X-ray source, or possibly a non-ionising radical-generating source, for example a UV source, but is preferably an electron beam, more preferably one providing a beam dose greater than 2 Mrads, preferably at least 5 Mrads, more preferably at least 10 Mrads, very preferably at least 15Mrads, into the material.

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It has been found that enhancements to the interfacial bond strength may be obtained by using certain additives. Additives preferably include a cross-linking promoter ("pro-rad") in the polyolefin-based material and/or in the PVDF-based material. Known cross-linking materials may be used, preferably methacrylate/acrylate based ones, and, very preferably, those of the type trimethylolpropanetrimethacrylate (TMPTM), in the polyolefin material and/or in the PVDF-based material.

Experimental results:

All results quoted in the tables below were obtained by testing pressed plaques of the two materials prepared by the usual polymer handling techniques, well known per se. The plaques were pressed together to bond them face-to-face and the bonded assembly was irradiated as indicated. Plaques were used for these demonstration experiments rather than wires, due to the relative ease of measuring bond strength on plaques. Conditions for these experiments were as follows:

Plaque dimensions: 150mm by 150mm by 0.85mm

Pressing temperature: 200°C

Pressing time: 2 minute preheat, 1 minute at pressure

Pressing pressure: 20-40 Tons over a 300mm by 300mm metal plate

Cooling conditions: 2 minutes between water cooled, 300mm by 300mm, metal plates, at a pressure as above

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Example of Effect of Radiation Dose on Bond strength developed between appropriate polyolefin and PVDF-based materials

Material 1	Material 2	Dose(Mrad)	Peel force (N)
EVA copolymer of 25wt% VA content	VDF/HFP copolymer of 10wt% HFP content +7.5wt% additives	0	0.5
Same as above	Same as above	15	40
EEA copolymer of 15wt% EA content	VDF/HFP copolymer of 10wt% HFP content	0	1
EEA copolymer of 15wt% EA content	VDF/HFP copolymer of 10wt% HFP content	8	24
EEA copolymer of 15wt% EA content	VDF/HFP copolymer of 10wt% HFP content	20	52
Ethylene/acrylic ester/maleic anhydride terpolymer of 19wt% acrylic ester content	VDF/HFP copolymer of 10wt% HFP content	0	<5
Ethylene/acrylic ester/maleic anhydride terpolymer of 19wt% acrylic ester content	VDF/HFP copolymer of 10wt% HFP content	20	21

Example of Effect of Percentage Comonomer in Ethylene Copolymer Material on bond strength to appropriate PVDF-based material after electron beam crosslinking

Material 1	Material 2	Dose(Mrad)	Peel (N)
EMA copolymer with 9wt% MA content	VDF/HFP copolymer of 10wt% HFP content +7.5wt% additives	20	4
EMA copolymer with 28wt% MA content	Same as above	20	45

Example of Effect of percentage Copolymer in a polyolefin polymer blend on bond strength with appropriate PVDF-based material after electron beam crosslinking

Material 1	Material 2	Dose(Mrad)	Peel force (N)
100% HDPE	VDF/HFP copolymer of 10wt% HFP content +7.5wt% additives	20	0
20% HDPE + 80% EEA copolymer of 15wt% EA content	Same as above	20	70

Example of Effect of PVDF-based material type on bond strength with appropriate polyolefin based material after electron beam crosslinking

Material 1	Material 2	Dose(Mrad)	Peel (N)
EVA copolymer with 25wt% VA content	PVDF homopolymer	15	4
As above	VDF/HFP copolymer of 10wt% HFP content	15	17.5

Example of Effect of the addition of Pro-rad in Olefinic Material on bond strength with appropriate PVDF-based material after electron beam crosslinking

Material 1	Material 2	Dose(Mrad)	Peel (N)
20% HDPE + 80% EEA copolymer of 15wt% EA content	VDF/HFP copolymer of 10wt% HFP content +7.5wt% additives	20	70
19% HDPE + 77%EEA copolymer of 15wt% EA content + 4% TMPTM pro-rad	Same as above	20	>130

Examples of Wire Construction

An electrical wire in which the insulation consists of two polymeric layers bonded together according to the present invention was made as follows:

The inner layer of insulation (i.e. nearer to the wire conductor) was a polyolefin-based material, consisting predominantly of (a) an EEA copolymer containing 15wt% EA and (b) HDPE in a weight ratio of approximately 8:2 copolymer:HDPE, with usual other additives present in smaller proportions including crosslinking promoters, stabilisers, antioxidants, pigments and process aids at a total level of 24wt%. This layer was pressure extruded onto the metallic conductor.

The outer layer of insulation consisted predominantly of a PVDF/HFP copolymer containing 10wt% HFP, which in this example contains a crosslinking promoter, and other known additives such as pigments, plasticisers, stabilisers, antioxidants and process aids in usual proportions totalling 7.5wt%.. This outer layer was pressure extruded in a separate operation onto the pre-formed inner layer. This coated wire product was then passed through an electron beam, and received a radiation dose of 20Mrads.

In a second example a wire was made as above, in which the crosslinking promoter in the inner layer was 4% TMPTM, and the the outer layer of insulation was comprised solely of the PVDF/HFP copolymer containing 10wt% HFP. This coated wire product was then passed through an electron beam, and received a radiation dose of 20 Mrads. This wire was subjected to the acetone immersion test, confirming that the insulation layers were significantly bonded together.

In a third example, a wire of the same construction as the second example was made by tandem pressure extrusion of the inner and outer insulation layers. This coated wire product was then passed through an electron beam, and received a radiation dose of 20 Mrads. This wire was subjected to the acetone immersion test, confirming that the insulation layers were significantly bonded together.

<u>Demonstration of Improved performance of wires constructed as in the second example above, relative to current commercially available wire.</u>

A wire of the above construction and manufacturing process (designated wire A) was compared with a market leading commercially available polyolefin/PVDF dual-walled wire (designated wire B) of the same dimensions, over a range of tests for wire robustness

relevant to harsh handling and end-use environments. The following results were obtained.

Example of scrape abrasion resistance improvement

Method: Equipment=conventional type wire scrape abrader, wire size $0.75mm^2$(conductor cross sectional area), blade type flat, width 3.5mm held perpendicular to wire, with 0.05mm radiused edges each side, applied load 1.8kg, stroke length 10cm, at 55 cycles/minute

Wire Type	No. of scrape cycles to abrade through PJ at 40°C
A	>800
B	272

Wire Type	No. of scrape cycles to abrade through PJ at 5°C
A	>1350
B	212

Example of cold impact resistance improvement

Method: wire size $6mm^2$(conductor cross sectional area), impact weight 800g, drop height 275mm onto anvil, anvil area impacting on wire of dimensions 7mm x 2mm widening to 3.4mm via 45° taper each side, ambient temperature 5°C. Visual detection of insulation crack propagation.

Wire Type	Result of cold impact test
A	No cracks in PJ propagate away from site of anvil impact
B	Severe cracks in PJ, >5 mm in length, propagate away from site of anvil impact. PJ starts to peel off core

Example of solvent resistance improvement

Method: wire size $0.75mm^2$, length of wire 60mm,acetone immersion length 75% of wire length, immersion time 1hour, temperature 23°C

Wire Type	Result of acetone immersion test

A	No separation/delamination of core and PJ, no cracking of either insulation layer observed
B	PJ wrinkled very severely along immersed length, cracking spontaneously in two places, and exposing 2-3mm of core